

Comparison of different methods for the prediction of retention times in programmed-temperature gas chromatography

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ABSTRACT

Four calculation methods that can be easily applied by simple BASIC programming on personal computers were compared for the prediction of the retention times of various substances during linear temperature programming with and without an initial isothermal period on polar and non-polar capillary columns. The methods are based on curve-fitting techniques or a numeric iterative integration approach (Simpson and trapezoid methods). The comparison with experimental data obtained in various programmed-temperature analyses showed that all the tested methods permit the prediction of the retention times. The computation times and deviations of the results are compared.

INTRODUCTION

The prediction of retention times in programmed-temperature gas chromatography (PTGC) starting from isothermal data has been carried out by different methods [1-12], some of them requiring a complex computational approach or a knowledge of thermodynamic quantities. Other papers were dedicated to the prediction of retention indices under PTGC conditions [1,4,11].

A direct approach that permits the calculation of linear temperature data starting from retention times measured at three isothermal temperatures by means of a curve-fitting technique to replace the inverse retention time function by a function that can be integrated was suggested by Said [13,14] and applied by us previously to the prediction of PTGC retention times of chlorobenzenes [15] with satisfactory approximation. Other integration methods using iterative proce-

dures (Simpson and trapezoid methods) were tested and compared with Said's methods. In order to test the performance of the programs for the prediction of the behaviour of compounds having different polarities and functional groups, a test mixture containing di- and tri-chlorobenzenes, nitro- and chloronitrobenzenes, chloroaniline and naphthalene was prepared and analysed on polar and non-polar capillary columns.

EXPERIMENTAL

A Model 3600 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a split-splitless injector and a flame ionization detector, was used for isothermal and PTGC analyses. A methylpolysiloxane DB-1 bonded phase non-polar capillary column, 0.25 μm film thickness (30 m X 0.32 mm I.D.) (J&W Scientific, Folsom, CA, USA), and a polyglycol DB-WAX polar capillary column (same dimensions) were used. The carrier gas was helium with a linear velocity

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ranging between 67 cm s⁻¹ (at 45°C) and 57 cm s⁻¹ (at 150°C). The isothermal data used for calculation were measured at 60, 80 and 120°C on the non-polar column and at 100, 120 and 140°C on the polar column in order to take into account the longer retention times of polar compounds on the latter column. Table I shows the composition of the test mixture, with the compounds listed in order of increasing retention time on the non-polar column. Molecular masses, boiling points, densities and melting points are also given.

The selected compounds belong to some of the polarity classes suggested by Ewell *et al.* [16]: compounds containing both donor atoms and active hydrogen (chloroanilines); molecules containing donor but no active hydrogen atom (nitro- and chloronitrobenzenes); and molecules with r-electron availability (naphthalene) more or less influenced by the inductive effect of halogens (chlorobenzenes). The mixture used therefore permits a severe test of the calculation methods to be carried out because, mainly on the polar column, co-eluting peaks and inversion of the elution order of some compounds are observed at different temperatures and during various programmed runs.

The retention times were measured with an accuracy of ±0.005 min by using a Varian DS-650 data system. The retention times automatically

calculated by the software were verified by using the interactive graphical data system in order to verify that the retention times (*t_R*) correspond to the maximum height of the peak. The same program also permitted the shape of each peak to be evaluated, in order to take into account the effect of the amount injected on the asymmetry and therefore on the deviation of the actual *t_R* with respect of the theoretical value at concentrations near zero.

CALCULATION METHODS

The methods that can be used in order to predict the retention of a given compound in a programmed-temperature run have the aim of calculating the retention temperature *θ_t*, *i.e.*, the column temperature at which the compound elutes from the column. The following equation, used by Said [14] and consistent with that derived by Habgood and Harris [17,18], must therefore be solved:

$$g = \int_{\theta_0}^{\theta_t} \frac{d\theta}{A + a \exp[b/(273 + \theta)]} = \int_{\theta_0}^{\theta_t} y(\theta) d\theta \quad (1)$$

where *g* is the temperature programming rate, *θ₀* is the initial temperature, *A* is the column dead time or gas hold-up time under isothermal conditions, in order to obtain the *θ_t* value. This integral has no analytical solutions and therefore

TABLE I

COMPOUNDS OF THE TEST MIXTURE LISTED IN ORDER OF ELUTION ON THE NON-POLAR DB-1 COLUMN, THEIR MOLECULAR MASSES *M*, BOILING POINTS *T_b*, DENSITIES *d*, AND MELTING POINTS *T_m*

No.	Compound	<i>M</i>	<i>T_b</i> (°C)	<i>d</i>	<i>T_m</i> (°C)
1	1,3-Dichlorobenzene	147.01	173	1.2884	-24.7
2	1,4-Dichlorobenzene	147.01	174	1.2475	53.1
3	1,2-Dichlorobenzene	147.01	180.5	1.3048	-1.7
4	Nitrobenzene	123.11	210.8	1.2037	5.7
5	2-Chloroaniline	127.57	208.84	1.2125	-1.4
6	1,3,5-Trichlorobenzene	181.45	208	—	63-64
7	1,2,4-Trichlorobenzene	181.45	213.5	1.4542	16.95
8	Naphthalene	128.19	218	1.0253	80.55
9	3-Chloroaniline	127.57	229.92	1.2161	-10.3
10	4-Chloroaniline	127.57	232	1.429	72.5
11	1,2,3-Trichlorobenzene	181.45	218-219	—	53-54
12	1-Chloro-3-nitrobenzene	157.56	235-236	1.343	46
13	1-Chloro-4-nitrobenzene	157.56	242	1.2979	83.6
14	1-Chloro-2-nitrobenzene	157.56	246	1.368	33.5-35

some approximate integration method must be used. Said [13,14] proposed two similar methods in order to obtain an analytical expression for the integral of eqn. 1 and, by using curve-fitting techniques, to replace the $y(\theta)$ with functions that can be integrated.

In the first method suggested by Said, henceforth denoted "Said A", a temperature θ , lower than the temperature θ_i of the inflection point of the function $y(\theta)$, so that $\theta = \theta_i - x$, is considered. In order to obtain an acceptable accuracy, the value of x should be between 50 and 100°C [14]. Empirically, a value of 75°C can be chosen for x and, by comparing the calculated and experimental results, one can see that in this instance the difference is negligible for all the compounds and for all linear programming rates.

In order to ensure that the difference between the predicted and actual programmed retention times of a set of compounds have the minimum value, the best x value should be obtained by the equation

$$x = 50 + 50 \left(\frac{\theta_i - 2\theta_0}{2\theta_0} \right) \quad (2)$$

This procedure was applied previously [15] and it was found that, whereas for megabore columns $x = 75^\circ\text{C}$ gives satisfactory precision, for narrow-bore columns the best correspondence between predicted and true retention times is obtained with x values near zero.

The second method proposed by Said ("Said B") does not employ the empirical x value, but iteratively calculates the intermediate constant values. The other two methods tested in this work in order to solve eqn. 1 are based on numerical integration algorithms, *i.e.*, the trapezoid method and the Simpson method [19-22]. In both instances the integral eqn. 1 is transformed into a sum of terms in order to verify the following:

$$g = \sum_{i=1}^N A(i) \quad (3a)$$

where, for the trapezoid method,

$$A(i) = \frac{\Delta\theta}{2} [y(\theta_{i-1}) + y(\theta_i)] \quad (4a)$$

and, for the Simpson method,

$$g = \sum_{i=1}^M A(i) \quad (3b)$$

where

$$A(i) = \frac{\Delta\theta}{3} [y(\theta_{2i-2}) + y(\theta_{2i-1}) + y(\theta_{2i})] \quad (4b)$$

θ being the increment of temperature values used for calculation (0.1°C). In practice, by starting with $i = 1$, the sums of eqns. 3 are calculated by increasing i by 1 at each iterative stop, and this procedure is repeated until eqns. 3 are verified for $i = N$ or M , the final value of θ_i being

$$\theta_i = \theta_0 + N \Delta\theta \quad (5a)$$

or

$$\theta_i = \theta_0 + 2M \Delta\theta \quad (5b)$$

for the trapezoid and the Simpson method, respectively.

The four methods were applied through BASIC programming on a IBM personal computer (PS2-286) and used to predict the retention times in various programmed runs with and without an initial isothermal period.

RESULTS AND DISCUSSION

The different elution orders on the two columns are shown in Table II, where the gross retention times, t_R , obtained in the various isothermal runs and the retentions relative to nitrobenzene, r , *i.e.*, the ratio between the adjusted retention times, t'_R , are reported, and are graphically illustrated in Fig. 1. Several changes in the elution order and coincidence of the retention times were observed. The Arrhenius plots, *i.e.*, the values of $\ln t'_R$ as a function of the reciprocal of the absolute analysis temperature, were linear with a standard deviation of better than 0.99 within the temperature range used on both columns. Only two isothermal runs should therefore be sufficient in order to obtain the input data for the calculation of PTGC retention times, because the third value required by the programs should be linearly interpolated on the Arrhenius plot.

Notwithstanding this, three values of isother-

mal retention times measured experimentally were used in order to evaluate the accuracy of the calculation methods for routine use when the raw data obtained from isothermal runs are directly input without any previous elaboration and control in order to calculate the retention times under PTGC conditions. If the integrating data system can be programmed to extract directly from the analysis reports the retention values of the identified peaks, and the data so obtained are used for further elaboration in the system itself, all the procedure can be made automatic without the need for an external computer and manual transfer of the retention data. The procedures to obtain these results obviously depend on the logic of the integrator used and therefore no further details on the BASIC programming and data transfer of the data system used are given here.

Table III shows some of the PTGC runs carried out in order to verify the performance of the four calculation methods, covering a wide range of possible combinations of initial isother-

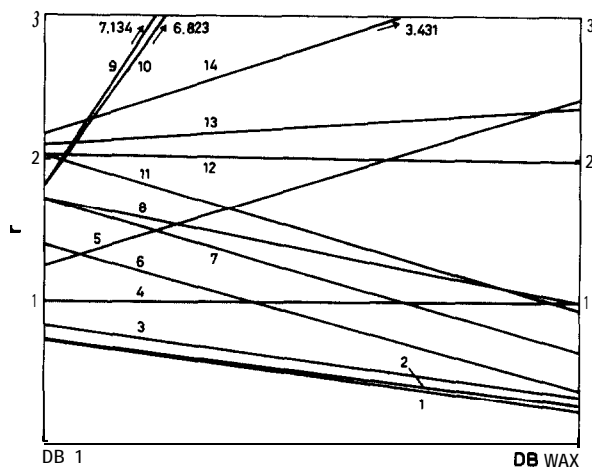


Fig. 1. Retention relative to nitrobenzene, r , at 120°C on non-polar DB-1 and polar DB-WAX capillary columns, showing the change in elution order and of retention times due to polarity. For numbers of compounds, see Table I. r Values at other temperatures are given in Table II.

mal temperature and time, programming rate and final temperature, Tables IV and V show the comparison of the values calculated with the four

TABLE II

EXPERIMENTAL GROSS RETENTION TIMES, t_R (min), AND RETENTIONS RELATIVE TO NITROBENZENE, r , IN THREE ISOTHERMAL RUNS ON DB-1 AND DB-WAX COLUMNS

See also Fig. 1 for r values.

Compound	DB-1 column (non polar)						DB-WAX column (polar)					
	60°C		80°C		120°C		100°C		120°C		140°C	
	t_R	r	t_R	r	t_R	r	t_R	r	t_R	r	t_R	r
1	4.254	0.619	2.345	0.653	1.273	0.724	2.687	0.207	1.835	0.236	1.442	0.269
2	4.403	0.645	2.400	0.676	1.273	0.724	2.975	0.239	1.963	0.267	1.522	0.307
3	5.018	0.753	2.655	0.781	1.340	0.829	3.574	0.306	2.226	0.331	1.644	0.366
4	6.424	1	3.188	1	1.450	1	9.804	1	4.976	1	2.971	1
5	8.938	1.441	4.063	1.360	1.607	1.245	26.636	2.875	10.848	2.429	5.380	2.152
6	9.819	1.596	4.464	1.525	1.702	1.393	3.916	0.344	2.399	0.373	1.726	0.405
7	12.874	2.133	5.557	1.975	1.911	1.718	6.530	0.635	3.540	0.651	2.276	0.668
8	13.185	2.187	5.718	2.041	1.911	1.718	9.804	1	4.976	1	2.971	1
9	14.288	2.381	5.841	2.091	1.953	1.783	87.259	9.630	30.188	7.134	12.438	5.525
10	14.512	2.420	5.931	2.129	1.953	1.783	83.048	9.161	28.907	6.823	12.000	5.316
11	15.926	2.668	6.653	2.426	2.111	2.030	9.310	0.945	4.735	0.941	2.847	0.941
12	16.436	2.758	6.744	2.463	2.111	2.030	20.356	2.176	9.051	1.991	4.735	1.843
13	17.404	2.928	7.063	2.595	2.158	2.103	24.545	2.642	10.598	2.368	5.289	2.108
14	18.014	3.035	7.265	2.678	2.191	2.154	42.797	4.676	14.969	3.431	6.610	2.739

^a See Table I.

TABLE III

PTGC RUNS USED TO EVALUATE THE AVERAGE PERFORMANCE OF THE FOUR CALCULATION METHODS ON DB-1 AND DB-WAX COLUMNS

Initial temperature, θ_0 ; length of initial isothermal period, t_i , and programming rate, g , are shown.

Column	Programmed run No.	θ_0 (°C)	t_i (min)	g (°C min ⁻¹)
DB-1	1	45	0	4
	2	45	0	5
	3	50	0	2
	4	50	0	3
	5	60	0	2
	6	70	0	2
	7	45	6	4
	8	50	3	5
	9	50	6	3
	10	60	6	4
	11	70	3	3
DB-WAX	1	45	0	5
	2	60	0	6
	3	45	6	4
	4	50	3	5
	5	70	2	6

methods and of the experimental retention time on non-polar and polar columns for two programmed runs, taken as examples. The parameter showing the performance of each method is the percentage deviation between the experimental, t_R , and calculated, t_R^c , values expressed as $E (\%) = 100|t_R^c - t_R|/t_R^c$. It is not possible to report here the E values for all the compounds of the test mixture obtained with all the programmed runs used and therefore the performance of the four calculation methods is compared by using the E values averaged over the whole set of programmed runs for each compound (Table VI) and over all the fourteen compounds contained in the test mixture for each programmed run listed in Table III (Table VII). The average E values for the DB-1 column are also plotted in Figs. 2 and 3.

The results obtained with the four methods are comparable. The low values show slight negative deviations from the experimental values, whereas high values show smaller but positive deviations. This behaviour, which can be also found in previously published papers [2,7,9,12] in which

TABLE IV

EXAMPLE OF THE VALUES OBTAINED THROUGH DIFFERENT PROGRAMMES COMPARED WITH THE EXPERIMENTAL DATA OBTAINED ON THE DB-1 COLUMN

PTGC parameters: initial temperature, $\theta_0 = 60^\circ\text{C}$; initial isothermal period, $t_i = 6$ min; programming rate, $g = 4^\circ\text{C min}^{-1}$. Identifying numbers in column 1 refer to Table I.

Compound ^a	Experimental t_R (min)	Said A		Said B		Trapezoid		Simpson	
		t_R (min)	E (%)	t_R (min)	E (%)	t_R (min)	E (%)	t_R (min)	E (%)
1	4.279	4.230	1.15	4.230	1.15	4.230	1.15	4.230	1.15
2	4.430	4.378	1.18	4.378	1.18	4.378	1.18	4.378	1.18
3	5.048	4.988	1.19	4.988	1.19	4.988	1.19	4.988	1.19
4	6.436	6.364	1.11	6.366	1.09	6.362	1.14	6.375	0.95
5	8.344	8.322	0.27	8.331	0.15	8.337	0.08	8.325	0.23
6	8.897	8.889	0.09	8.899	0.02	8.912	0.17	8.925	0.31
7	10.418	10.446	0.26	10.462	0.42	10.462	0.43	10.475	0.55
8	10.571	10.615	0.41	10.629	0.55	10.612	0.39	10.625	0.51
9	10.915	10.934	0.17	10.961	0.42	10.987	0.66	10.975	0.55
10	11.003	11.029	0.23	11.056	0.48	11.062	0.54	11.075	0.65
11	11.598	11.649	0.44	11.673	0.65	11.687	0.77	11.675	0.66
12	11.732	11.782	0.43	11.811	0.67	11.812	0.69	11.825	0.79
13	12.036	12.089	0.44	12.121	0.71	12.112	0.64	12.125	0.74
14	12.220	12.273	0.43	12.308	0.72	12.312	0.76	12.325	0.86

^a See Table I.

TABLE V

EXAMPLE OF THE VALUES OBTAINED THROUGH DIFFERENT PROGRAMMES COMPARED WITH THE EXPERIMENTAL DATA OBTAINED ON THE DB-WAX COLUMN

PTGC parameters: initial temperature, $\theta_0 = 60^\circ\text{C}$; no initial isothermal period; programming rate, $g = 6^\circ\text{C min}^{-1}$.

Compound ^a	Experimental t_R (min)	Said A		Said B		Trapezoid		Simpson	
		t_R (min)	E (%)	t_R (min)	E (%)	t_R (min)	E (%)	t_R (min)	E (%)
1	5.310	5.207	1.94	5.195	2.17	5.242	1.29	5.250	1.13
2	5.782	5.752	0.52	5.762	0.35	5.792	0.17	5.785	0.02
3	6.475	6.552	1.18	6.593	1.82	6.592	1.80	6.585	1.67
4	10.776	10.755	0.19	10.801	0.23	10.792	0.15	10.785	0.07
5	14.382	14.366	0.11	14.458	0.53	14.458	0.53	14.450	0.47
6	6.954	6.883	1.03	6.923	0.44	6.908	0.66	6.920	0.54
7	9.115	9.077	0.42	9.131	0.18	9.108	0.07	9.120	0.02
8	10.776	10.756	0.19	10.801	0.23	10.792	0.15	10.785	0.07
9	18.312	18.312	0.00	18.296	0.09	18.442	0.71	18.450	0.76
10	18.164	18.161	0.02	18.151	0.07	18.292	0.70	18.285	0.66
11	10.562	10.538	0.23	10.586	0.23	10.592	0.28	10.585	0.20
12	13.609	13.572	0.27	13.640	0.23	13.642	0.24	13.650	0.30
13	14.301	14.223	0.54	14.304	0.02	14.308	0.05	14.320	0.11
14	15.357	15.550	1.28	15.645	1.87	15.675	2.07	15.685	2.12

^a See Table I.

TABLE VI

VALUES OF E (%) AVERAGED OVER THE PROGRAMMED RUNS LISTED IN TABLE III FOR ALL OF THE COMPOUNDS IN TABLE I, OBTAINED WITH THE FOUR CALCULATION METHODS ON NON-POLAR (DB-1) AND POLAR (DB-WAX) COLUMNS

Compound ^a	Said A		Said B		Trapezoid		Simpson	
	DB-1	DB-WAX	DB-1	DB-WAX	DB-1	DB-WAX	DB-1	DB-WAX
1	0.74	2.87	0.77	2.94	1.08	2.35	1.32	2.31
2	0.79	0.32	0.77	0.32	0.91	0.41	1.00	0.40
3	0.57	1.48	0.68	2.45	0.85	2.23	0.90	2.20
4	0.46	0.32	0.68	0.60	0.84	0.47	0.94	0.46
5	0.24	0.34	0.59	0.80	0.84	0.80	0.86	0.80
6	0.24	1.04	0.65	0.32	0.86	0.53	0.93	0.54
7	0.31	0.40	0.83	0.57	1.02	0.32	1.03	0.29
8	0.44	0.32	0.92	0.60	0.94	0.47	0.91	0.46
9	0.20	0.34	0.85	0.31	0.94	0.87	0.91	0.85
10	0.21	0.35	0.92	0.31	1.00	0.85	0.98	0.85
11	0.39	0.33	0.99	0.62	1.00	0.51	0.99	0.47
12	0.34	0.31	0.99	0.59	1.00	0.58	0.96	0.58
13	0.35	0.41	1.02	0.45	1.03	0.41	1.05	0.46
14	0.36	1.40	1.05	2.32	1.05	2.45	1.17	2.43

^a See Table I.

different calculation programs were used, therefore do not depend on the computation method but on the choice of the coefficients (**A**, **a** and **b**) of the generally accepted starting eqn. 1. The

literature [13,14] suggests that three isothermal runs are sufficient to permit a correct evaluation of these constants. As the same procedure for the calculation of the constants was used as a

TABLE VII

VALUES OF E (%) AVERAGED OVER THE FOURTEEN COMPOUNDS IN TABLE I, OBTAINED WITH THE FOUR CALCULATION METHODS IN THE PROGRAMMED RUNS LISTED IN TABLE III ON NON-POLAR (DB-1) AND POLAR (DB-WAX) COLUMNS

Programmed run No. ^a	Said A		Said B		Trapezoid		Simpson	
	DB-1	DB-WAX	DB-1	DB-WAX	DB-1	DB-WAX	DB-1	DB-WAX
1	0.11	0.81	1.00	1.08	1.17	1.01	1.11	1.02
2	0.47	0.57	1.47	0.60	1.66	0.63	1.67	0.58
3	0.44	1.49	0.83	1.38	0.93	1.18	0.94	1.16
4	0.21	0.56	0.85	1.19	1.07	1.16	1.08	1.14
5	0.37	0.64	0.61	0.71	0.71	0.84	0.89	0.85
6	0.39		0.61		0.72		0.93	
7	0.32		0.79		0.81		0.82	
8	0.61		1.09		1.28		1.28	
9	0.59		0.76		0.76		0.76	
10	0.56		0.67		0.70		0.74	
11	0.36		0.52		0.69		0.73	

^a See Table III.

starting point for the four calculation methods, in order to avoid introducing a difference in the evaluation of the performance of the four methods, the similar deviations obtained confirm that the problem comes from the basic equation. In fact, a strong reduction in the temperature interval used for each iteration step and therefore an increase in the precision of the approximation do not change substantially the accuracy

of the final results. Also, the choice of the three temperatures of the basic isothermal runs influences the values of A and the subsequent calculations, and it was found that the accuracy of the final results increases when the range of the programmed run lies within that of the isothermal runs.

The E values are lower for the non-polar column, but the polar column also shows average

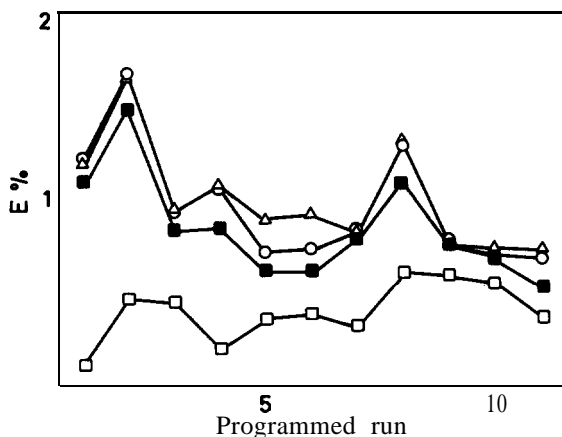


Fig. 2. Values of E averaged over the fourteen compounds in Table I for eleven different programmed runs on the DB-1 column. Methods: \square = Said A; \blacksquare = Said B; \circ = trapezoid; \triangle = Simpson.

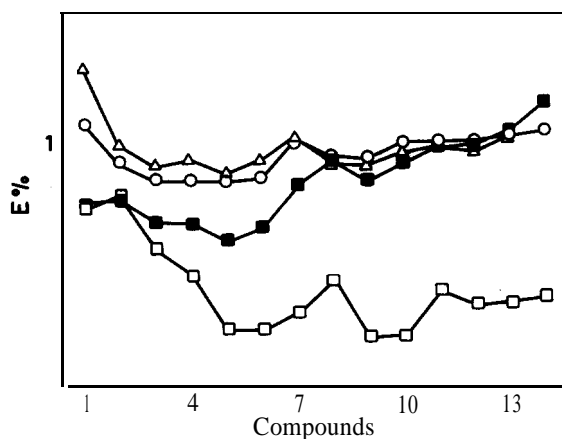


Fig. 3. Values of E averaged over eleven programmed runs on the DB-1 column (see Table III). Methods: \square = Said A; \blacksquare = Said B; \circ = trapezoid; \triangle = Simpson.

errors smaller than 3%. The scatter of the data does not depend on the type of programmed runs, as no systematic difference connected to the initial temperature, programming rate, etc., is shown by Table VII and Fig. 2. Table VI and Fig. 3, on the other hand, show that early-eluting compounds have a greater influence on the average E values, as affected by a greater uncertainty, probably because the measurement of short t_R comparable to the gas hold-up time is difficult and therefore both the isothermal data used to input the program and the PTGC data measured experimentally are less accurate. This is confirmed by Fig. 4, showing the r^2 values obtained with the equation

$$r^2 = \frac{[\sum (t_R^c - \bar{t}_R^c)(t_R^e - \bar{t}_R^e)]^2}{\sum (t_R^c - \bar{t}_R^c)^2 \sum (t_R^e - \bar{t}_R^e)^2}$$

where \bar{t}_R^c and \bar{t}_R^e are the calculated and experimental retention times averaged over the eleven temperature-programmed runs. The value of r^2 is a measure of the best fit between the experimental and calculated values and should be equal to unity for a perfect fit of the values. The results found for the four calculation methods are better than 0.9995 for the compounds eluted after nitrobenzene with gross retention times t_R at the highest isothermal temperature greater than 1.5 and 3 min on the non-polar and polar column, respectively (see Table II). The

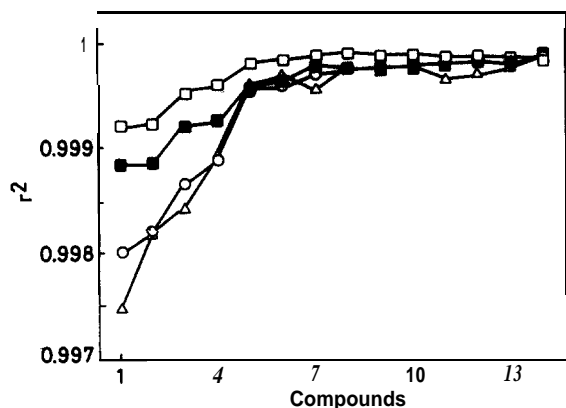


Fig. 4. Values of r^2 as a function of the fourteen compounds in Table I, calculated with the following methods: \square = Said A; \blacksquare = Said B; \circ = trapezoid; \triangle = Simpson.

results for nitrobenzene and early-eluting peaks show a lower precision, but r^2 values greater than 0.997 indicate a precision high enough for practical purposes.

The computation time necessary to obtain the results with the four programming methods, after the input of the data, was calculated by taking into account the average time required to obtain the calculated retention time of one of the compounds for a given programmed run. This procedure requires $4.6 \cdot 10^{-3}$ s with the Said A, 0.22 s with the Said B, 0.20 s with the trapezoid and 0.13 s with the Simpson method. All these times are so short with respect of the keyboard input time that the use of any of the methods is equivalent from the practical point of view. The complexity and length of the BASIC programs for the four methods are similar.

The Said A method, owing to the simplification due to the choice of a default x value, is more rapid if operated on a personal computer and can also be applied with a simple calculating machine, as it does not require iterative procedures. The iterative methods, moreover, are subject to appreciable fluctuations in the prediction of the early-eluting peaks, as they are more influenced by possible errors in the measurement of short retention times during isothermal runs at high temperature.

The application of the Said B method, i.e., the iterative calculation of the intermediate constants, may fail to give the t_R values in a reasonable computation time if a double precision calculation (with sixteen decimal places) is carried out, because the speed of convergence of the calculation may be too small at this degree of precision. If, by means of a proper adjustment of the program, the convergence was required only to the tenth decimal place, all our experimental data correctly permitted the PTGC t_R to be calculated. This means that, by working with single precision (seven decimal places), convergence of the calculation to the exact values is obtained.

CONCLUSIONS

The prediction of programmed-temperature retention data gives comparable accuracies on

both non-polar and polar capillary columns and for compounds belonging to different homologous series and to many polarity classes.

The comparison of the experimental data with those predicted with the four calculation methods showed that, by using only three isothermal runs as the source of the input data and simple BASIC computer programming, satisfactory accuracy in the prediction of programmed-temperature analyses with various linear speeds and with or without an isothermal period can be obtained. The programming methods are almost equivalent from the point of view of the accuracy and precision of the results, are based on known iterative calculation procedures and can be selected depending on the programming experience of the gas chromatographer, as they do not require sophisticated software.

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